FUNCTIONAL ELECTROLYTE FOR LITHIUM-ION BATTERIES

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Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 98 days.

Appl. No.: 13/787,433
Filed: Mar. 6, 2013

Prior Publication Data

Int. Cl.
H01M 6/16 (2006.01)
C07C 43/205 (2006.01)
H01M 10/052 (2010.01)
H01M 10/0569 (2010.01)
H01M 10/0567 (2010.01)

U.S. Cl.
CPC C07C 43/2055 (2013.01); H01M 10/052 (2013.01); H01M 10/0569 (2013.01); H01M 10/0567 (2013.01)

Field of Classification Search
USPC ................................. 429/326, 327, 330
See application file for complete search history.

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ABSTRACT

Functional electrolyte solvents include compounds having at least one aromatic ring with 2, 3, or 4 substituents, at least one of which is a substituted or unsubstituted methoxy group, at least one of which is a tert-butyl group and at least one of which is a substituted or unsubstituted polyether or poly(ethylene oxide) (PEO) group bonded through oxygen to the aromatic ring, are provided.

18 Claims, 9 Drawing Sheets
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FIG. 1

[Graph showing cyclic voltammograms at different scan rates]
FIG. 2
FIG. 3

- Charge capacity
- Discharge capacity

Capacity (mAh)

Cycle number
FIG. 4

Plot showing voltage (V) over time (h). The voltage remains constant at approximately 2.5 V throughout the duration of the measurement, which spans from 0 to 300 hours.
FIG. 6

Current (1E-5 A) vs. E (Volts) for different RS-9 voltages: 500mV/S, 200mV/S, 100mV/S, 50mV/S, 20mV/S, 10mV/S, 5mV/S.
FIG. 7
FIG. 8

![Graph showing capacity over cycle number. The graph plots capacity (mAh) against cycle number. There are two lines: one for charge capacity indicated by squares and the other for discharge capacity indicated by circles. The capacity values range from 0 to 4 mAh, with cycles numbered from 0 to 50.]
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STATEMENT OF GOVERNMENT INTEREST

The United States Government has rights in this invention pursuant to Contract No. DE-AC02-06CH11357 between the U.S. Department of Energy and UC Chicago Argonne, LLC, representing Argonne National Laboratory.

FIELD

The present technology generally relates to compounds that provide intrinsic overcharge protection in lithium ion batteries, electrical double-layer capacitors and other electrochemical devices.

BACKGROUND

Lithium ion batteries (LIB) were conceived and developed in Japan by Asahi Kasei Co. and first commercialized by Sony Co. in 1991, and soon this novel energy storage technology had drawn tremendous attention from academic and industry communities alike. With many extensive research and engineering efforts conducted, lithium-ion batteries have become the most popular power source for portable electronic devices, such as, but not limited to, cell phones, mp3 players, and laptop computers. In addition, applications for use in the hybrid vehicle (HEV) and plug-in hybrid electric vehicle (PHEV) are being actively investigated. However, the improvements in battery performance must also be mindful of safety issues. When more energy or capacity is stored in the cell, the system becomes more thermodynamically unstable. For secondary lithium-ion batteries, dangerous results could be triggered under certain situations such as shortage, elevated temperature and overcharge.

Overcharge is a battery condition where electrical flow is forced through a cell after the capacity of the cell has been already been reached. Overcharge is one of the more common factors that could lead to serious safety issues in lithium-ion batteries. The phenomenon is most likely to occur during the charging of a battery pack. Due to the manufacturing processes, there will always be a weakest cell with the lowest capacity in the one battery pack. During charging, the weak cell will always reach its full capacity before the other cells and without triggering the voltage monitor of the charger because the voltage of the full pack is still within the normal range. But the weak cell is none-the-less in a state of overcharge. As a result, extra electricity will build up on the surface of the electrodes instead of being stored, thereby dramatically increasing the potential of the cathode. As the charging is continued, the potential will go beyond the electrochemical window of the electrolyte and cause various reactions of the electrolyte. For example, oxidation of the electrolyte may occur and thereby trigger other reactions. The cell may end up in a thermal runaway, or even result in an explosion.

SUMMARY

In one aspect, a functional electrolyte solvent is provided, which includes a compound having the formula I,

In the compound have the formula I, R$^1$ is

R$^2$ and R$^3$ are each independently H, F, Cl, Br, I, alkyl, or a polyether group; R$^4$ and R$^5$ are each independently H, F, Cl, Br, I, CN, NO$_2$, alkyl, haloalkyl, phosphate, polyether groups; R$^{14}$ is H, alkyl or haloalkyl; m is an integer from 1 to 20, inclusive; and n is an integer from 1 to 16, inclusive.

In some embodiments, R$^1$ is selected from

In formulas II-1 through II-4, each of R$^6$-R$^{13}$ is independently H, F, Cl, Br, I, CN, NO$_2$, alkyl, haloalkyl, phosphate, polyether groups; R$^{14}$ is H, alkyl or haloalkyl group; m is an integer from 1 to 20, inclusive; and n is an integer from 1 to 16, inclusive.

In some embodiments, the compound of formula I has the structure
where R² and R³ are each independently H, F, Cl, Br, I, alkyl, or a polyether group. In other embodiments, the compound of formula I has the structure

where R² and R³ are each independently H, F, Cl, Br, I, alkyl, or a polyether group.

In one aspect, the functional electrolyte solvent is 1-(2-methoxyethoxy)ethoxy-4-methoxy-2,5-di-tert-butyl-benzene, 1-[2-(2-methoxyethoxy)ethoxy]-4-methoxy-2,5-di-tert-butyl-benzene, or a mixture thereof.

In another aspect, an electrolyte is provided, which includes the functional electrolyte solvent and an alkali metal salt. In some embodiments, the functional electrolyte solvent is a redox active material and has a redox potential of 3 to 5 V versus Li/Li⁺. In some embodiments, the concentration of the functional electrolyte solvent in the electrolyte is from 0.0005 wt% and 60 wt%. In some embodiments, the alkali metal salt is a lithium salt. In some embodiments, the alkali metal salt includes Li(C₂O₄)₂[B], Li(C₂O₄)BF₄, Li(N(C₂SO₃)₂)₂, Li(N(C₂SO₃)₂C₂SO₃)₂, or Li[N(SO₂C₂F₂)₂], or a mixture of any two or more thereof.

In one aspect, the electrolyte further includes a polar aprotic solvent. In some embodiments, the polar aprotic solvent is selected from ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, methyl ethyl carbonate, dimethyl ether, gamma butyrolactone, or a mixture of any two or more thereof.

In some embodiments, the polar aprotic solvent is selected from ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, methyl ethyl carbonate, dimethyl ether, gamma butyrolactone, or a mixture of any two or more thereof.

In one aspect, the electrolyte further includes an electrolyte stabilizing additive that is a substituted or unsubstituted spirocyclic hydrocarbon containing at least one oxygen atom and at least one alkynyl or alkynyl group.

In yet another aspect, an electrochemical device is provided, which includes a cathode, an anode and an electrolyte which includes a functional electrolyte solvent. In some embodiments, the electrochemical device is a lithium secondary battery. The cathode is a lithium metal oxide cathode; the anode is a carbon or lithium metal anode; and the anode and cathode are separated from each other by a porous separator.

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing and other objects, aspects, features and advantages of the disclosure will become more apparent and better understood by referring to the following description taken in conjunction with the accompanying drawings, in which:

FIG. 1 illustrates a cyclic voltammogram of an electrolyte that includes 0.01 M 1-methoxy-4-(2-methoxyethoxy)-2,5-di-tert-butyl-benzene in 1.2M LiPF₆ in EC/EMC (3:7 by weight) at various scan rates using a Pt/Li/Li three-electrode system (Pt working electrode, Li counter electrode and Li reference electrode), according to Example 1.

FIG. 2 is an overcharge test voltage profile of cells using MCMB and LFP as electrodes and containing 0.1 M 1-methoxy-4-(2-methoxyethoxy)-2,5-di-tert-butyl-benzene in 1.2M LiPF₆ in EC/EMC (3:7 by weight), charging rate is C/10 and overcharge 100%, according to Example 1.

FIG. 3 is an overcharge test capacity profile of cells using MCMB and LFP as electrodes and containing 0.1 M 1-methoxy-4-(2-methoxyethoxy)-2,5-di-tert-butyl-benzene in the electrolyte of 1.2M LiPF₆ in EC/EMC (3:7 by weight), charging rate is C/10 and overcharge 100%, according to Example 1.

FIG. 4 is an overcharge test voltage profile of cells using MCMB and LFP as electrodes and containing 0.2 M 1-methoxy-4-(2-methoxyethoxy)-2,5-di-tert-butyl-benzene in the electrolyte of 1.2M LiPF₆ in EC/EMC (3:7 by weight), charging rate is C/5 and overcharge 100%, according to Example 1.

FIG. 5 illustrates capacity retention profiles of MCMB/LiFePO₄ cell containing 0.2 M 1-methoxy-4-(2-methoxyethoxy)-2,5-di-tert-butyl-benzene in the electrolyte of 1.2M LiPF₆ in EC/EMC (3:7 by weight) during the course of 0-3100 h. Charging rate is C/10 and overcharge is 100%, according to Example 1.

FIG. 6 illustrates a cyclic voltammogram of an electrolyte that includes 0.01 M 1-methoxy-4-(2-methoxyethoxy)-2,5-di-tert-butyl-benzene in Gen 2 electrolyte at various rates using a Pt/Li/Li three-electrode system, according to Example 2.

FIG. 7 is an overcharge test voltage profile of cells using MCMB and LFP as electrodes and containing 0.4 M 1-methoxy-4-(2-methoxyethoxy)ethoxy)-2,5-di-tert-butyl-benzene, charging rate is C/2 and overcharge 100%, according to Example 2.

FIG. 8 is an overcharge test capacity profile of cells using MCMB and LFP as electrodes and containing 0.4 M 1-methoxy-4-(2-methoxyethoxy)ethoxy)-2,5-di-tert-butyl-benzene, charging rate is C/2 and overcharge 100%, according to Example 2.

FIG. 9 illustrates capacity retention profiles of LFP/LTO cells using electrolyte of Gen 2: 1-methoxy-4-[2-(2-methoxyethoxy)ethoxy]-2,5-di-tert-butyl-benzene 2:1 by weight. The cells were cycled at room temperature from 1.5 V to 2.1 V at C/10 rate, according to Example 2.

DETAILED DESCRIPTION

In the following detailed description, reference is made to the accompanying drawings, which form a part thereof. In the drawings, similar symbols typically identify similar components, unless context dictates otherwise. The illustrative embodiments described in the detailed description, drawings and claims are not meant to be limiting. Other embodiments may be utilized, and other changes may be made, without departing from the spirit or scope of the subject matter presented here. It will be readily understood that the aspects of the present disclosure, as generally described herein, and illustrated in the figures, can be arranged, substituted, combined and designed in a wide variety of different configurations, all of which are explicitly contemplated and made part of this disclosure.

Various embodiments are described hereinafter. It should be noted that the specific embodiments are not intended as an exhaustive description or as a limitation to the broader aspects discussed herein. One aspect described in conjunction with a particular embodiment is not necessarily limited to that embodiment and can be practiced with any other embodiment(s).
As used herein, “about” will be understood by persons of ordinary skill in the art and will vary to some extent depending upon the context in which it is used. If there are uses of the term which are not clear to persons of ordinary skill in the art, given the context in which it is used, “about” will mean up to, plus or minus 10% of the particular term.

The use of the terms “a,” “an” and “the” and similar referents in the context of describing the elements (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., “such as”) provided herein, is intended merely to better illuminate the embodiments and does not pose a limitation on the scope of the claims unless otherwise stated. No language in the specification should be construed as indicating any non-art claimed element as essential.

In general, “substituted” refers to an alkyl, alkenyl, alkynyl, aryl, or other group, as defined below (e.g., an alkyl group) in which one or more bonds to a hydrogen or carbon atom contained therein are replaced by a bond to non-hydrogen or non-carbon atoms. Substituted groups also include groups in which one or more bonds to a hydrogen(s) atom are replaced by one or more bonds, including double or triple bonds, to a heteroatom. Thus, a substituted group will be substituted with one or more substituents, unless otherwise specified. In some embodiments, a substituted group is substituted with 1, 2, 3, 4, 5, or 6 substituents. Examples of substituent groups include: halogen(s) (i.e., F, Cl, Br, and I); hydroxyls; alkoxys; alkenoxys; alkyloxys; aryloxys; alkynyls; heterocyclos; esters; urethanes; oximes; hydroxylamines; alkoxyamines; thiools; sulfides; sulfoxides; sulfoxyls; sulfonamides; amines; N-oxides; hydrazines; hydrazides; hydrazonates; azides; amides; amines; amidines; guanidines; enamines; imines; isocyanates; iso(thiocyanates); cyanates; thiocyanates; nitro groups; nitriles (i.e., CN); and the like.

As used herein, “alkyl” groups include straight chain and branched alkyl groups having from 1 to 20 carbon atoms, and typically from 1 to 12 carbons or, in some embodiments, from 1 to 8 carbon atoms. As employed herein, “alkyl groups” include cycloalkyl groups as defined below. Unless expressly indicated otherwise, alkyl groups may be substituted, or unsubstituted, and if no designation is used, it is assumed that the alkyl group may be either substituted or unsubstituted. Examples of straight chain alkyl groups include methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, and n-octyl groups. Examples of branched alkyl groups include, but are not limited to, isopropyl, sec-butyl, t-butyl, neopentyl, and isopentyl groups. Representative substituted alkyl groups may be substituted one or more times with, for example, amino, thio, hydroxy, cyano, alkoxys and/or halogen groups such as F, Cl, Br, and I groups. In some embodiments, the term haloalkyl is an alkyl group having one or more halo groups. In some embodiments, haloalkyl refers to a per-haloalkyl group.

Cycloalkyl groups are cyclic alkyl groups such as, but not limited to, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, and cyclooctyl groups. In some embodiments, the cycloalkyl group has 3 to 8 ring members, whereas in other embodiments the number of ring carbon atoms range from 3 to 5, 6 or 7. Unless expressly indicated otherwise, cycloalkyl groups may be substituted or unsubstituted, and if no designation is used, it is assumed that the cycloalkyl group may be either substituted or unsubstituted. Cycloalkyl groups further include poly cyclic cycloalkyl groups such as, but not limited to, norbornyl, adamantyl, bornyl, camphenyl, isocamphenyl, and carenyl groups, and fused rings such as, but not limited to, decalyl, and the like. Cycloalkyl groups also include rings that are substituted with straight or branched chain alkyl groups as defined above. Representative substituted cycloalkyl groups may be mono-substituted or substituted more than once, such as, but not limited to: 2,2-; 2,3-; 2,4-; 2,5-; or 2,6-disubstituted cyclohexyl groups or mono-, di-, or tri-substituted norbornyl or cycloheptyl groups, which may be substituted with, for example, alkyl, alkoxy, amino, thio, hydroxy, cyano, and/or halo groups.

Alkenyl groups are straight chain, branched or cyclic alkyl groups having 2 to about 20 carbon atoms, and further including at least one double bond. In some embodiments alkenyl groups have from 1-12 carbons or, typically, from 1-8 carbon atoms. Unless expressly indicated otherwise, alkenyl groups may be substituted or unsubstituted, and if no designation is used, it is assumed that the alkenyl group may be either substituted or unsubstituted. Alkenyl groups include, for instance, vinyl, propenyl, 2-butenyl, 3-butenyl, isobutenyl, cyclohexenyl, cyclopentenyl, cyclohexadienyl, butadienyl, pentadienyl, and hexadienyl groups among others. Alkenyl groups may be substituted similarly to alkyl groups. Divalent alkenyl groups, i.e., alkenyl groups with two points of attachment, include but are not limited to, CH—CH—CH₂, C—CH₂, or C—CH₂CH₃.

As used herein, “aryl” groups are cyclic aromatic hydrocarbons that do not contain heteroatoms. Aryl groups include monocyclic, bicyclic and polycyclic ring systems. Thus, aryl groups include, but are not limited to, phenyl, azulenyl, heteroaryl, biphenylphenyl, indacenyl, fluorenyle, phenanthrenyl, triphenylphenyl, pyrenyl, naphthacenyl, chrysene, biphenylanthracenyl, indenyl, indanyl, pentalenyl, and naphthyl groups. In some embodiments, aryl groups contain 6-14 carbons, and in others from 6-12 or even 6-10 carbon atoms in the ring portions of the groups. The phrase “aryl groups” includes groups containing fused rings, such as fused aryl-aryl-arylic ring systems (e.g., indanyl, tetrahydrophenyl, and the like). Aryl groups may be either substituted and unsubstituted aryl groups and if no designation is used, it is assumed that the aryl group may be either substituted or unsubstituted. Substituted aryl groups may be mono-substituted or substituted more than once. For example, monosubstituted aryl groups include, but are not limited to, 2, 3-, 4-, 5-, or 6-substituted phenyl or naphthyl groups, which may be substituted with substituents such as those listed above.

As defined herein, an “aromatic” group include those groups identified as aryl groups, but where aryl group is used to define substituent groups on a primary structure, the aromatic ring is the primary structure. Thus, aromatic rings include monocyclic, bicyclic and polycyclic ring systems. Aromatic rings include, but are not limited to, benzene rings, azulene rings, biphenylene rings, indacene rings, fluorene rings, pyrene rings, phenanthrene rings, triphenylene rings, naphthalene rings, and anthracene rings. As used herein the term heteroaryl is a polycyclic aromatic ring containing one or more nitrogen atoms. In some embodiments, aromatic rings contain 6-14 carbons, and in others from 6-12 or even 6-10 carbon atoms in the ring portions. Aromatic rings may be either substituted or unsubstituted aryl groups and if no designation is used, it is assumed that the aromatic ring may be either substituted or unsubstituted. Substituted aryl groups may be mono-substituted or substituted more than once. For example, monosubstituted aryl groups include, but are not
limited to 2-, 3-, 4-, 5-, or 6-substituted phenyl or naphthyl
groups, which may be substituted with substituents such as those listed above.

As used herein, “aralkyl” groups are alkyl groups as defined above in which a hydrogen or carbon bond of an alkyl group is replaced with a bond to an aryl group as defined above. In some embodiments, aralkyl groups contain 7-20 carbon atoms, 7-14 carbon atoms or 7-10 carbon atoms. Unless expressly indicated otherwise, aralkyl groups may be substituted or unsubstituted, and if no designation is used, it is assumed that the aralkyl group may be either substituted or unsubstituted.

As used herein, “heterocyclyl” groups includes non-aromatic ring compounds containing 3 or more ring members, of which one or more is a heteroatom such as, but not limited to, N, O, and S. In some embodiments, heterocyclyl groups include 3-20 ring members, whereas other such groups have 3-6, 3-10, 3-12, or 3-15 ring members. Heterocyclyl groups encompass unsaturated, partially saturated and saturated ring systems, such as, for example, imidazolyl, imidazoliny1 and imidazolidinyl groups. Unless expressly indicated otherwise, heterocyclyl groups may be substituted or unsubstituted, and if no designation is used, it is assumed that the heterocyclyl group may be either substituted or unsubstituted. Heterocyclyl groups include, but are not limited to, aziridinyl, azetidinyl, pyrrolidinyl, imidazolidinyl, pyrazolidinyl, thiazolidinyl, tetrahydrothiophenyl, tetrahydrofurany1, dioxy1, furanyl, thiophenyl, pyrroly1, pyrrolinyl, imidazolyl, imidazoliny1, pyrazolyl, pyrazoliny1, triazolyl, tetrazolyl, oxazolyl, isoxazolyl, thiazolyl, thiazoliny1, isothiazolyl, thiazolopyranyl, oxadiazolyl, pyridyl, pyridinyl, morpholinyl, thiomorpholinyl, tetrahydroprpyranyl, tetrahydroprpyryl, oxathiane, dioxiane, diathi1any1, pyrany1, pyridyl, pyridinyl, pyridazinyl, pyrazinyl, triazinyl, dihydropyridyl, dihydrothiopyrany1, dihydrothiopyrily1, homopiperazinyl, quinuclidinyl, indolyl, indoliny1, isoindoliny1, azaindolyl, piperony1, piperidinyl, indazolyl, indazoliny1, benzimidazolyl, benzimidazoliny1, benzothiazolyl, benzothiazoliny1, benzimidazolyl, benzimidazoliny1, benzoxazolyl, benzothiazolyl, benzoxothiazolyl, benzothiadiazolyl, benzof1-3]dioxolyl, pyrazolopyrily1, imidazopyriny1,aza-benzimidazolyl, triazolopyrily1, isoxazolopyrily1, purinyl, xanthinyl, adeninyl, guaninyl, quinoxalinyl, isoquinolinyl, quinolinyl, quinazolinyl, quinoxalinyl, cinchoninyl, phthalazinyl, naphtpyridinyl, pteridinyl, thianaphthenyl, dihydrobenzothiazolyl, dihydrobenzofuranyl, dihydroindolyl, dihydrobenzoxoxindolyl, tetrahydroindolyl, tetrahydrodiazolyl, tetrahydrobenzimidazolyl, tetrahydrobenzothia-

diazoxolyl, tetrahydroprpyranopyrily1, tetrahydroprpyridopyrily1, tetrahydrothiazolopyrily1, tetrahydrothiazolopyrily1, triazolopyrily1, tetrahydroquinolinyl groups. Representative substituted heterocyclyl groups may be mono-substituted or substituted more than once, such as, but not limited to, pyridyl or morpholinyl groups, which are 2-, 3-, 4-, 5-, or 6-substituted, or disubstituted with various substituents such as those listed above.

As used herein, “heteroaryl” groups are aromatic ring compounds containing 5 or more ring members, of which one or more is a heteroatom such as, but not limited to, N, O, and S. Unless expressly indicated otherwise, heteroaryl groups may be substituted or unsubstituted, and if no designation is used, it is assumed that the heteroaryl group may be either substituted or unsubstituted. Heteroaryl groups include, but are not limited to, groups such as pyrroly1, pyrazolyl, triazolyl, tetrazolyl, oxazolyl, isoxazolyl, thiazolyl, pyridyl, pyridazinyl, pyrimidinyl, pyrazinyl, thiophenyl, benzothiphienyl, furanly1, benzo[1,3]dioxolyl, pyrazolopyrily1, imidazopyriny1,aza-benzimidazolyl, triazolopyrily1, isoxazolopyrily1, purinyl, xanthinyl, adeninyl, guaninyl, quinoxalinyl, isoquinolinyl, quinolinyl, quinazolinyl, quinoxalinyl, cinchoninyl, phthalazinyl, naphtpyridinyl, pteridinyl, thianaphthenyl, dihydrobenzothiazolyl, dihydrobenzofuranyl, dihydroindolyl, dihydrobenzoxoxindolyl, tetrahydroindolyl, tetrahydrodiazolyl, tetrahydrobenzimidazolyl, tetrahydrobenzothia-

diazoxolyl, tetrahydroprpyranopyrily1, tetrahydroprpyridopyrily1, tetrahydrothiazolopyrily1, tetrahydrothiazolopyrily1, triazolopyrily1, tetrahydroquinolinyl groups. Representative substituted heterocyclyl groups may be mono-substituted or substituted more than once, such as, but not limited to, pyridyl or morpholinyl groups, which are 2-, 3-, 4-, 5-, or 6-substituted, or disubstituted with various substituents such as those listed above.

In some embodiments, the functional electrolyte solvents include a compound having the formula I:

\[
\text{CH}_3
\]

R1

R2

R3

R4

In formula I, R3 is H, F, Cl, Br, I, alkyl, or a polyether, R3 is H, F, Cl, Br, I, alkyl, or a polyether, and R4 may be a group of formula II, which is:
In formula II, R² is H, F, Cl, Br, I, CN, NO₂, alkyl, haloalkyl, phosphate, or a polyether; R³ is H, F, Cl, Br, I, CN, NO₂, alkyl, haloalkyl, phosphate, or a polyether; R⁴ is H, alkyl or haloalkyl; m is an integer from 1 to 20, inclusive; and n is an integer from 1 to 16, inclusive. In some embodiments, R¹ is H, F, Cl, Br, I, C₁-C₈ alkyl, or a polyether; R² is H, F, Cl, Br, I, C₁-C₈ alkyl, or a polyether; R³ is H, F, Cl, Br, I, CN, NO₂, C₁-C₈ alkyl, C₁-C₈ haloalkyl, phosphate, or a polyether; R⁴ is H, F, Cl, Br, I, CN, NO₂, C₁-C₈ alkyl, C₁-C₈ haloalkyl, phosphate, or a polyether; R⁵ is H, C₁-C₈ alkyl or C₁-C₈ haloalkyl; m is an integer from 1 to 20, inclusive; and n is an integer from 1 to 16, inclusive. In some embodiments, R¹ is H, F, Cl, methyl, or ethyl; R² is H, F, Cl, methyl, or ethyl; R³ is H, F, Cl, methyl, or ethyl; R⁴ is H, F, Cl, methyl, or ethyl; or a polyether; R⁵ is H, F, Cl, methyl, or ethyl; or a polyether; R⁶ is H, methyl, or ethyl; m is an integer from 1 to 20, inclusive; and n is an integer from 1 to 16, inclusive.

In some embodiments, R¹ is a group of formulas II-1 through II-5. Formulas II-1 through II-4 include:

In formulas II-1 through II-4, each of R⁸-R¹₃ is independently H, F, Cl, Br, I, CN, NO₂, alkyl, haloalkyl, phosphate, or a polyether group; R¹⁴ is H, alkyl or haloalkyl group; m is an integer from 1 to 20, inclusive; and n is an integer from 1 to 16, inclusive. In some embodiments, each of R⁸-R¹₃ is independently H, F, Cl, Br, I, C₁-C₈ alkyl, a C₁-C₈ haloalkyl, or a polyether group; R¹⁴ is H, C₁-C₈ alkyl or a C₁-C₈ haloalkyl group; m is an integer from 1 to 20, inclusive; and n is an integer from 1 to 16, inclusive. In some embodiments, each of R⁸-R¹₃ is independently H, F, Cl, Br, I, C₁-C₈ alkyl, a C₁-C₈ haloalkyl, or a polyether group; R¹⁴ is H, C₁-C₈ alkyl or a C₁-C₈ haloalkyl group; m is 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10; and n is an integer from 1 to 20, inclusive. In some embodiments, each of R⁸-R¹₃ is independently H, F, Cl, methyl or ethyl; R¹⁴ is H, methyl, or ethyl; m is 1, 2, 3, 4, 5, 6, 7, 8, or 9; and n is 1, 2, 3, 4, 5, 6, 7, or 8.

In some embodiments, R¹ is a group of formula II-2, R², R³, R⁴, R⁵, R⁶, and R⁷ are H; R¹⁴ is methyl, or ethyl; and m is 1, 2, 3, 4, 5, 6, 7, or 8.

In some embodiments, the compound of formula I has the structure

wherein R² is H, F, Cl, Br, I, alkyl, or a polyether group, and R¹ is H, F, Cl, methyl, ethyl, or a polyether group. In some embodiments, R² is H, F, Cl, methyl, ethyl, or a polyether group, and R¹ is H, F, Cl, methyl, ethyl, or a polyether group. In some embodiments, R² is H, and R¹ is H.

In some embodiments, wherein the compound of formula I has the structure

wherein R² is H, F, Cl, Br, I, alkyl, or a polyether group, and R¹ is H, F, Cl, methyl, ethyl, or a polyether group. In some embodiments, R² is H, F, Cl, methyl, ethyl, or a polyether group. In some embodiments, R² is H, and R¹ is H.

In some embodiments, the fractional electrolyte solvent is 1-methoxy-4-[2-(2-methoxyethoxy)ethoxy]-2,5-di-tert-butyl-benzene, 1-methoxy-4-[2-(2-methoxyethoxy)ethoxy]-2,5-di-tert-butyl-benzene, or a mixture thereof. In other embodiments, the functional electrolyte solvent is 1-methoxy-4-[2-(2-ethoxyethoxy)ethoxy]-2,5-di-tert-butyl-benzene, 1-methoxy-4-[2-(2-(2-methoxyethoxy)ethoxy)ethoxy]-2,5-di-tert-butyl-benzene, 1-methoxy-4-[2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)ethoxy]-2,5-di-tert-butyl-benzene.

The functional electrolyte solvents are typically non-aqueous. As used herein, non-aqueous means that the water content of the electrolyte or solvent is minimal, or only an adventitious amount of water is present. In some embodiments, less than 20 parts per million (ppm) of water is present. In other embodiments, less than 15 ppm of water is present. In various other embodiments, less than 10 ppm, or even less than 5 ppm, of water is present. Substantially non-aqueous electrolyte solvents also include embodiments where no water is present.

In one embodiment, the functional electrolyte solvents are redox active materials and have a redox potential of about 3.5 V to about 5.0 V. In some embodiments, the functional electrolytes have a redox potential of about 3.6 V to about 4.6 V.
In some embodiments, the functional electrolyte solvents are liquid redefix active materials or redefix shuttles that may not only be used as electrolyte solvents or co-solvents, but they may also be configured to provide overcharge protection to the devices they are included in, e.g., lithium-ion batteries.

In another aspect, an electrolyte is provided, which includes a functional electrolyte solvent and an alkaline metal salt.

The functional electrolyte solvents are present in the electrolyte in concentrations suitable the concentration of the functional electrolyte solvent in the electrolyte is from 0.0005 wt % and 90 wt %.

In some embodiments, the electrolyte further includes a polar aprotic solvent. Suitable polar aprotic solvents are known in the art and include, but are not limited to ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, dimethyl ether, gamma butyrolactone, or a mixture of any two or more thereof.

Any of the functional electrolyte solvents described above may be used in an electrochemical device having an anode (negative electrode), a cathode (positive electrode), and the electrolyte. Examples of such functional devices include all kinds of primary batteries, secondary batteries, fuel cells, biofuel cells, flywheels, solar cells, and capacitors such as supercapacitor devices. In some embodiments, the electrochemical cell is a primary cell. In some embodiments, the primary cell that is a lithium/MnO2 battery or Li/poly (carbon monofluoride) battery. In some embodiments, the electrochemical device is a lithium secondary battery. In some embodiments, the secondary battery is a lithium battery, a lithium-ion battery, a lithium-sulfur battery, a lithium-air battery, a sodium ion battery, or a magnesium battery. In one embodiment, the electrochemical device is a lithium-ion battery.

A variety of salts, including alkali metal salts, may be employed in the electrochemical device, and will be known to those of skill in the art. In some embodiments, e.g., in lithium-ion batteries, the alkaline metal salt is a lithium salt. Illustrative salts are LiF, LiClO4, (C2H5)4Li, LiBF4, LiPF6, LiCF3SO3N, Li(NCOS)2CF3, LiC2F5SO3C2H4, LiPF6, LiClO4, LiBF4, LiCF3SO3N, Li(NCOS)2CF3, LiC2F5SO3C2H4, or LiPF6.

In some embodiments, the lithium metal salt is other than Li[(C2O4)2]2, LiI, Li(C2O4)BF4, and the electrolyte further comprises about 0.001 wt % to about 8 wt % of an electrode stabilizing additive that is Li[(C2O4)2]2, LiI, Li(C2O4)BF4, or a mixture thereof.

A variety of negative electrodes or anodes may be employed in the electrochemical devices such as lithium-ion batteries. Representative negative electrodes include Li, Ti, Sn, Zr, or Mo; and, the electrolyte further comprises 3.45 A×d=0.002-3.54 A and existing in forms such as powders, flakes, fibers, or spheres (e.g., mesocarbon microbeads); and other materials that will be familiar to those skilled in the art, and combinations thereof.

A variety of current collectors may be employed in the electrochemical devices such as lithium-ion batteries. Often, the negative and positive electrodes will be carried on the current collector, with the current collector serving as a support. The current collector may also be an adjacent material, e.g., a shell of a lithium-ion button cell. A variety of arrangements will work, so long as the negative and positive electrodes make suitable electrical contact with their associated current collector.

Some guidelines may aid in selecting the negative electrode material. The current collector. To prevent lithium capture during recharging, the negative electrode current collector has a lithium alloying potential below the negative electrode's minimum normal operating potential. Thus, the negative electrode current collector selection will be guided in part by the negative electrode selection. To discourage or prevent current collector dissolution during overdischarging, it may be helpful to employ a negative electrode current collector having a dissolution potential above the shuttle reduction potential. Thus, the negative electrode current collector selection may also be guided in part by the shuttle selection.

Representative negative electrode current collectors include aluminum, copper, stainless steels (e.g., 300 series and 400 series stainless steels), titanium, tantalum, niobium, INCONEL™ nickel chromium alloys (commercially available from International Nickel Co.), combinations thereof and other materials that will be familiar to those skilled in the art. Aluminum has a lithium alloying potential of about 0.3 V vs Li. Most of the other listed materials are believed to have lithium alloying potentials below 0 V. Copper is believed to have a dissolution potential below about 4.0 V. Most of the other listed materials are believed to have dissolution potentials above 4.0 V. The current collector may be monolithically throughout, or may have a surface or exposed layer whose composition is different from the composition of the underlying current collector material. Aluminum appears to offer especially good performance.

When the negative electrode has a larger irreversible first cycle capacity loss than that of the positive electrode, the positive electrode will normally remain at an elevated potential during overdischarge. Its current collector will be held near the same elevated potential and will not be susceptible to lithium capture during recharging or dissolution during overdischarging. Accordingly there are fewer constraints on selection of the positive electrode current collector. Representative positive electrode current collectors include aluminum, stainless steels (e.g., 300 series and 400 series stainless steels), titanium, tantalum, niobium, INCONEL™ alloys, combinations thereof and other materials that will be familiar to those skilled in the art.

A variety of positive electrodes or cathodes may be employed in the electrochemical devices such as lithium-ion batteries. Illustrative cathode materials include, but are not limited to, spinel, olivine, carbon-coated olivine, LiMnPO4, LiMn2O4, LiCoPO4, LiCoO2, LiFePO4, LiNiO2, LiNi1/3Co1/3Mn1/3O2, LiNiO2, LiNiO2, LiFeO2, LiFeO2, LiMnO2, LiNiO2, LiNiO2, and combinations thereof. Other cathode materials include materials transition metal oxides as disclosed in U.S. Pat. Nos. 5,458,324; 5,890,365; 6,143,269; 6,964,828; 7,078,128; 7,211,237; and 6,680,145; and in U.S. Patent Application Publication Nos. 2003/0072048; 2004/0121234; 2004/0179993; and 2006/045144; and in combinations of any two or more such materials.

The negative or positive electrode may contain additives such as will be familiar to those skilled in the art, e.g., carbon...
black for negative electrodes and carbon black, flake graphite and the like for positive electrodes.

The negative and positive electrode capacities may optionally be selected to provide an excess negative electrode capacity. This enables the fractional electrolyte solvents operating as redox active materials or redox shuttle materials as to provide overcharge protection. About 10 to about 20% excess negative electrode capacity is recommended. Lesser or greater excess negative electrode capacities may be employed if desired.

A variety of charge carrying media may be employed in the electrolyte. Exemplary media are liquids or gels capable of solubilizing sufficient quantities of the alkali metal salt and the functional electrolyte solvent so that a suitable quantity of charge can be transported from the positive electrode to negative electrode. Exemplary charge carrying media can be used over a wide temperature range, e.g., from about 30°C to about 70°C, without freezing or boiling, and are stable in the electrochemical window within which the cell electrodes and shuttle operate. Representative charge carrying media include ethylene carbonate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, buty- lene carbonate, vinylene carbonate, fluoroethylene carbonate, fluoroethylene carbonate, γ-butyrolactone, methyl difluorooacetate, ethyl difluorooacetate, dimethoxyethane, diglyme (bis(2-methoxyethyl)ether), combinations thereof and other materials that will be familiar to those skilled in the art.

In addition to the functional electrolyte solvents which operate as redox active materials or redox shuttle materials, a variety of additional redox chemical shuttles may be employed in electrochemical devices. The shuttle, if present, will have an electrochemical potential above (e.g., slightly above) the positive electrode's maximum normal operating potential. Thus, the shuttle selection may be guided in part by the positive electrode selection. As a general numeric guide, the shuttle may, for example, have a redox potential about 0.3 to 0.6 V above the positive electrode’s maximum normal operating potential, e.g., about 3.7 to about 4.7 V vs. Li/Li⁺, about 3.7 to about 4.4 V vs. Li/Li⁺, about 3.7 to about 4.2 V vs. Li/Li⁺, or about 3.7 to about 4.0 V vs. Li/Li⁺. For example, LiFePO₄, positive electrodes having a recharge plateau around 3.45 V vs. Li/Li⁺, and exemplary shuttles for use with such electrodes may have a redox potential from about 3.75 to about 4.05 V vs. Li/Li⁺. Similarly, LiMnPO₄ and LiMn₂O₄ electrodes have a recharge plateau around 4.1 V vs. Li/Li⁺, and exemplary shuttles for use with such electrodes may have a redox potential from about 4.4 to about 4.7 V vs. Li/Li⁺.

Illustrative additional redox shuttles include, but are not limited to, anisole, substituted anisoles (or methoxybenzenes) such as 2-methylanisole, 2-ethylisopropyl, 2-tert-butyl-anisole, 3,5-tet-butyli-anisole, 4-tet-butyl-anisole, 2-bromoanisole, 4-bromoanisole, 2,4,6-tribromoanisole, 3,5 dichloroanisole, 2,4,6-trichloroanisole, 4-bromo-2-fluoroanisole, 1-cyclopropyl-2-methoxybenzene, 1-nitro-3-tet-butyl-2-methoxybenzene, 2-cyan-3-tet-butyl-2-methoxybenzene, 1,4-di-tet-butyl-2-methoxybenzene, 5-tet-butyl-1,3-dinitro-2-methoxybenzene, 1-(benzaldehyde)-2-bromo-4-methoxybenzene, 1,3,5-tri-tet-butyl-2-methoxybenzene, 1-(2-ethylhexyl)-4-methoxybenzene, 1-benzoyl-4-methoxybenzene, 4-methoxybenzene, 1-(2-etethoxybenzyl)oxo-1-methoxybenzene and 2-tet-butyli-anisole; anisole substituted phthalates such as 4-methoxyphthalate; anisole-substituted catechols such as 3-methoxy catechol; substituted di-alkoxybenzenes such as 2-methyl-1,4-dimethoxybenzene, 2,3-dimethyl-1,4-dimethoxybenzene, 2,5-dimethyl-1,4-dimethoxybenzene, 2,6-dimethyl-1,4-dimethoxybenzene, 2,3,5,6-tetramethyl-1,4-dimethoxybenzene, 4-methyl-1,2-dimethoxybenzene, 2,3,5,6-tetramethylyl-1,4-dimethoxybenzene, 2,3-diethyl-1,4-dimethoxybenzene, 2,5-diethyl-1,4-dimethoxybenzene, 2,6-diethyl-1,4-dimethoxybenzene, 2,3,6-triethyl-1,2-dimethoxybenzene, 2,3,5,6-tetraethyl-1,4-dimethoxybenzene, 4-ethyl-1,2-dimethoxybenzene, 2,5-disopropyl-1,4-dimethoxybenzene, 2-tet-butyl-1,4-dimethoxybenzene, 2,3-di-tet-butyl-1,4-dimethoxybenzene, 2,5-di-tet-butyl-1,4-dimethoxybenzene, 3,6-dinitro-1,4-dimethoxybenzene, 2,5-di-tet-butyl-3,6-di-cyano-1,4-dimethoxybenzene, 2,5-di-tet-butyl-1,4-dimethoxybenzene, 2,5-di-tet-butyl-1,4-diacetoxybenzene, 2,5-dicyclohexyl-1,4-dimethoxybenzene, 4-tet-butyl-1,2-dimethoxybenzene, 4,5-di-tet-butyl-1,2-dimethoxybenzene and 4,5-di-tet-butyl-1,2 diethoxybenzene; substituted alkoxynaphthalenes such as 4,8-di-tet-butyl-1,5-dimethoxynaphthalene; polycyclic compounds such as 1,3,5,7-tetra-isopropylbenzene, compounds such as 1,5,7-octahydroanthracene and 9,10-dimethoxy-1,4,5,8-dieno-1,2,3,4,5,6,7,8-octahydroanthracene and 9,10-dimethoxy-1,4,5,8-dieno-1,2,3,4,5,6,7,8-octahydroanthracene.

In some embodiments, the non-aqueous electrolytes which include the functional electrolyte solvent may also include an electrode stabilizing additive to protect the electrodes from degradation. See, e.g., co-pending U.S. Pat. Nos. 7,968,235, and 7,748,497. Thus, electrolytes can include an electrode stabilizing additive that can be reduced or polymerized on the surface of a negative electrode to form a passivation film on the surface of the negative electrode. Likewise, electrolytes can include an electrode stabilizing additive that can be oxidized or polymerized on the surface of the positive electrode to form a passivation film on the surface of the positive electrode. In some embodiments, electrolytes further include mixtures of the two types of electrode stabilizing additives. The additives are typically present at a concentration of about 0.01% to 8 wt%.

In some embodiments, an electrode stabilizing additive is a substituted or unsubstituted linear, branched or cyclic hydrocarbon comprising at least one oxygen atom and at least one aryl, alkenyl or alkynyl group. The passivating film formed from such electrode stabilizing additives may also be formed from a substituted aryl compound or a substituted or unsubstituted heterocyclic compound where the additive comprises at least one oxygen atom. Alternatively, a combination of two additives may be used. In some such embodiments, one additive is selective for forming a passivating film on the cathode to prevent leaching of metal ions and the other additive is selective for passivating the anode surface to prevent or lessen the reduction of metal ions at the anode.

Representative electrode stabilizing additives include 1,2-diviny furano, 1,3-buta styrene carbonate, 1-vinylaze din-2-one, 1-vinylaziridine-2-one, 1-vinylpiperidin-2-one, 1-vinylpyroldin-2-one, 2,4-diviny-1,3-dioxane, 2 amino-3 vinylcyclohexanone, 2-amino-3 vinylcyclohexanone, 2-amino-4-vinylcyclohexanone, 2-amino-5-vinylcyclohexanone, 2,4-lactone-2-vinylxylol, 2-vinylxylol, 2-vinylxylol, 2-vinylxylol, 2-vinylxylol, 2-vinylxylol, 2-vinylxylol, 2-vinylxylol, 2-vinylxylol, 2-vinylxylol, 2-vinylxylol, 2-vinylxylol, 2-vinylxylol, 2-vinylxylol, 2-vinylxylol.
ate, divinyl ethylene silicate, divinyl ethylene sulfide, divinyl ethylene sulfite, divinyl methoxyprazine, divinyl methylene phosphate, divinyl propylene carbonate, ethyl phosphate, methoxy-o-terphenyl, methyl phosphate, oxetan-2-yl vinylamine, oxiranylmethyl vinylamine, vinyl carbonate, vinyl crotonate, vinyl cyclopentanone, vinyl ethyl-2-furoate, vinyl ethylene carbonate, vinyl ethylene silicate, vinyl ethylene sulfite, vinyl methacrylate, vinyl phosphate, vinyl-2-furoate, vinylpropylene oxepine, vinylpyridine oxide, \( \beta \)-vinyl-2-butylalcohol, or a mixture of any two or more thereof. In some embodiments, the electrode stabilizing additive may be a cyclostrophosphate that is substituted with F, alkoxy, alkenoxy, arylox, methoxy, alkoxy groups, or combinations thereof. For example, the additive may be a (divinyl)-(methoxy)(trifluoro)cyclostrophosphate, (trimethyl(methyl)carbonyl)methylcyclostrophosphate, (vinyl)(methoxy)(tetrafluoro)cyclostrophosphate, (aryllox)(tetrafluoro) methoxy)cyclostrophosphate, (diaryllox)(trifluoro) (methoxy)cyclostrophosphate compounds, or a mixture of two or more such compounds. In some embodiments, the electrode stabilizing additive is vinyl ethylene carbonate, vinyl carbonate, or 1,2-diphenyl ether, or a mixture of any two or more such compounds.

Other representative electrode stabilizing additives may include compounds with phenyl, naphthyl, anthracenyl, pyrrolyl, oxazolyl, furanyl, indolyl, carbazolyl, imidazolyl, or thiophenyl groups. For example, electrode stabilizing additives may be aryloxypyrole, arloxoy ethylene sulfate, arl oxopyrazine, arl oxocarbazole trivinyl phosphate, arl oxoethyl-2-furoate, arl oxo-terphenyl, arloxoy pyridazine, butyl-aryl ether, vinyl diphend northwest, (tetrahydro-furan-2-yl)vinylamine, divinyl methoxybyrindine, methoxy-4-vinyl pyrole, vinyl methoxycarbazole, vinyl methoxy piperidine, vinyl methoxypyrazine, vinyl methyl carbonate-allylamine, vinyl pyridazine, 1,4-dinitrilmidazole, 3,5-vinyltetrahydrofuran, divinyl furan, divinyl methoxy furan, divinylpyrazine, vinyl methoxy imidazole, vinylmethoxy pyrole, vinyltetrahydrofuran, 2,4-diyvinyl isoazolone, 3,4 divinyl-1-methylpyrrole, arl oxophenyl carbonate, arloxoy-piperidine, arl oxotetrahydrofuran, 2-aryl cyclicpropane, 2-diarylurea, 4-allyllisouole, arl oxocarbazole, arl oxo-2-furoate, arl oxocrotonate, arl oxocyclobutane, arl oxocyclopentanone, arl oxocyclopropanone, arl oxocyclophosphaxazine, arl oxo-ethylene silicate, arl oxo-ethylene sulfate, arl oxo-ethylene silicate, arl o xo-ethylene sulfite, arloxoy-methacrylate, arl oxophosphate, arl oxopyrrole, arl oxquinoline, diaryloxycyclophosphazine, diarylox ethylene carbonate, diarylox furan, diarylox methyl phosphate, diarylox-butyl carbonate, diarylox-crotonate, diarylox-diphenyl ether, diarylox-ethyl silicate, diarylox ethylene silicate, diarylox ethylene sulfite, diaryloxethylene silicate, diarylox-phenyl carbonate, diaryloxpropylene carbonate, diphenyl carbonate, diphenyl diarylox silicate, diphenyl divinyl silicate, diphenyl ether, diphenyl silicate, divinyl methoxypiperylene ether, divinyl phenyl carbonate, methoxycarbazole, or 2,4-dimethyl-6-hydroxy-pyrindine, vinyl methoxquinoline, pyridazine, vinyl pyridazine, quinoline, vinyl quinoline, pyridine, vinyl pyridine, indole, vinyl indole, triethanolamine, 1,3-dimethyl butadiene, butadiene, vinyl ethylene carbonate, vinyl carbonate, imidazole, vinyl imidazole, piperidine, vinyl piperidine, pyrimidine, vinyl pyrazine, isoquinoline, vinyl isoquinoline, quinoxaline, vinyl quinoline, biphylene, 1,2-dipheny1 ether, 1,2-diphenylethanone, o terphenyl, N-methylpyrrole, naphthalene, or a mixture of any two or more such compounds.

In other embodiments, electrode stabilizing additives include, but are not limited to, substituted or unsubstituted spirocyclic hydrocarbons containing at least one oxygen atom and at least one alkenyl or alkynyl group. For example, such stabilizing additives include those having Formula III:

\[
A^1 - C^1 - G^1 - G^2 - A^3 - A^4 - A^5 - G^6 - A^7 - A^8 - A^9 - A^{10} - A^{11} - A^{12} - A^{13} - A^{14} - A^{15} - G^{15} - A^{16} - G^{16}
\]

wherein A1, A2, A3, A4 are independently O or CR1R2R3; provided that A1 is not O when G1 is O, A2 is not O when G2 is O, A3 is not O when G3 is O, and A4 is not O when G4 is O; G1, G2, G3, and G4 are independently O or CR1R2R3; provided that G1 is not O when A1 is O, G2 is not O when A2 is O, G3 is not O when A3 is O, and G4 is not O when A4 is O; R1, R2, and R3 are independently a substituted or unsubstituted divalent alkyl, aryl, or alkynyl group.

Representative examples of Formula III include, but are not limited to, 3,9-divinyl-2,4,8,10-tetraoxaspiro[5.5]undecane, 3,9-divinyl-2,4,8-trioxaspiro[5.5]undecane, 3,9-divinyl-2,4-dioxaspiro[5.5]undecane, 3,9-diethyldielen-2,4,8,10-tetraoxaspiro[5.5]undecane, 3,9-diethyldielen-2,4,8,10-tetraoxaspiro[5.5]undecane, 3,9-diethyldielen-2,4,8,10-tetraoxaspiro[5.5]undecane, 3,9-diethyldielen-1,5,7,11-tetraoxaspiro[5.5]undecane, 3,9-diethyldielen-1,5,7,11-tetraoxaspiro[5.5]undecane, 3,9-diethyldielen-1,5,7,11-tetraoxaspiro[5.5]undecane, or a mixture of any two or more such compounds. Furthermore, mixtures of any two or more electrode stabilizing additives may also be used in the electrolytes of the present technology.

In some embodiments, the electrode stabilizing additive is an anion receptor. In some embodiments, the anion receptor is a Lewis acid. In other embodiments, the anion receptor is a borane, a boronate, a borate, or a mixture of any two or more such compounds.

In some embodiments, the anion receptor is a compound of the Formula IV:

\[
R^{17} - B - R^{18} - R^{19} - R^{17}
\]

where, each R17, R18, and R19 are independently halogen, alkyl, aryl, halogen-substituted alkyl, halogen-substituted aryl, or OR1; or any two of R17, R18, and R19, together with the atoms to which they are attached, form a heterocyclic ring having 5-9 members, and R17 is at each occurrence independently alkyl, aryl, halogen-substituted alkyl, or halogen-substituted aryl.

In some embodiments, the anion receptors include, but are not limited to, tri(proplyl)borate, tris(1,1,1,3,3,3-hexafluoro-2-propan-2-yl)borate, tris(1,1,1,3,3,3-hexafluoro-2-phenyl-propan-2-yl)borate, tris(1,1,1,3,3,3-hexafluoro-2-trifluoromethylene propan-2-yl)borate, triphenyl borate, tris(4-fluoroaryl)borate, tris(2,4-difluorophenyl)borate, tris(2,3,5,6-tetrafluorophenyl)borate, tris(pentafluorophenyl)borate, tris(3,5-trifluoromethyl)phenyl)borate, tris(3,5-bis(trifluoromethyl)phenyl)borate, tris(pentafluorophenyl)borate, or a mixture of any two or more thereof. Further suitable additives include 2-(2,4-difluorophenyl)-4-fluoro-1,3,2-benzodioxaborole, 2-(3-trifluoromethyl phenyl)-4-fluoro-1,3,2-benzodioxaborole, 2,5-bis(trifluoromethyl)phenyl-4-fluoro-1,3,2-benzodioxaborole, 2-(4-fluorophenyl)-tetrafluoro-1,3,2-benzodioxaborole, 2-(2,4-difluorophenyl)-tetrafluoro-1,3,2-benzodioxaborole, 2-(pentfluorophenyl)-tetrafluoro-1,3,2-benzodioxaborole, 2-(2,4-difluorophenyl)-tetrafluoro-1,3,2-
benzodioxaborole, 2-(2-trifluoromethyl phenyl)-tetrafluoro-1,3,2-benzodioxaborole, 2,5-bis(trifluoromethyl phenyl)tetrafluoro-1,3,2-benzodioxaborole, 2-phenyl-4,4,5,5-tetra (trifluoromethyl)-1,3,2-benzodioxaborolane, 2-(3,5-difluoroethyl)-4,4,5,5-tetra (trifluoromethyl)-1,3,2-benzodioxaborolane, 2,5-pentafluoro(phenyl)tetrafluoro-1,3,2-benzodioxaborolane, bis(1,1,2,3,3-hexafluoropropropyl)phenyl-boronicate, bis(1,1,2,3,3-hexafluoropropropyl)pentamethylcyclopentadiene, or a mixture of any two or more such compounds.

In some embodiments, each anion receptor is present at a concentration of about 0.001 to about 10 wt %.

Other additives may also be used within the electrolyte and electrochemical devices. For example, compounds such as, but not limited to, Li,Hf,X2,H,H2, Li,Hf,10,H10,H, or a mixture of two or more of such compounds may be included in the electrolytes. In such compounds, X is O, CH2, F, Cl, Br, or I, and n is an integer from 0 to 12, and n is an integer from 0 to 10. Such compounds may be present from about 0.001 to 15 wt %. In some embodiments, the compounds are present from about 0.001 to about 8 wt %.

In some embodiments, the electrode stabilizing additive is any of the above electrode stabilizing additives, or a mixture of any two or more such additives.

In some embodiments, the electrolyte is a gel electrolyte which includes the functional electrolyte solvent, at least one aprotic solvent; at least one lithium salt; at least one crosslinking agent, at least one monofunctional monomeric compound, and at least one radical reaction initiator. In some embodiments, the gel electrolyte may also include other electrode stabilization additives and other electrolyte additives.

In some embodiments, suitable crosslinking agents may be represented by Formula V:

\[
R^{20}-\text{CH} \equiv \text{C} \text{(O)CH}_{2} \text{CH}_{2} \text{CH} \equiv \text{C} \text{(O)CH}_{2} \text{CH}_{2} \text{CH}-\text{R}^{23}
\]

where \( R^{20}, R^{21}, R^{22}, \) and \( R^{23} \) are each independently \( H \), an alkyl group having from 1 to 12 carbon atoms, or an alkenyl group having from 2 to 12 carbon atoms; and \( X \) is a hydrogen, methyl, or ethyl group, and \( n \) is an integer from 1 to 15. Monofunctional monomeric compounds may be used for the control of the crosslinking density of the gel electrolyte. Suitable monofunctional monomeric compounds include those of Formula VI:

\[
R^{24}-\text{CH} \equiv \text{C} \text{(O)CH}_{2} \text{CH}_{2} \text{CH} \equiv \text{C} \text{(O)CH}_{2} \text{CH}_{2} \text{CH}-\text{R}^{26}
\]

where \( R^{24} \) is an alkyl group having from 1 to 12 carbon atoms; \( R^{25} \) and \( R^{26} \) are each independently \( H \), an alkyl group having from 1 to 12 carbon atoms, or an alkenyl group having from 2 to 12 carbon atoms; \( X \) is \( H \), methyl or ethyl group; and \( q^{*} \) is an integer from 1 to 20.

Crosslinking agents and monofunctional monomeric compounds provide a physical framework, or gel, after crosslinking to host the liquid phase. Variation of the amount of the crosslinking agent and monofunctional monomeric compound in the gel may impact the conductivity of the gel electrolyte due to changes in viscosity. Lower viscosity gels are prepared with higher concentrations of monofunctional monomeric compounds, as compared to the concentration of monofunctional monomeric compounds used for higher viscosity gels. Without being bound by theory, higher viscosity gels may be expected to have lower electrochemical conductivity, while lower viscosity gels may be expected to have higher electrochemical conductivity. However, other electrochemical properties of the gel electrolyte, or an electrochemical cell prepared with the gel electrolyte, such as oxidation potential and reduction potential, are not expected to be impacted.

Polymerization of crosslinking agents and monofunctional monomeric compounds are known to those of skill in the art. For example, monofunctional monomeric compounds may be polymerized by thermal and photoinitiation. Representative thermal initiators include, but are not limited to, an azo compound, a peroxide compound, bismaleimide, or a mixture of any two or more thereof. One example of an azo compound is azoisobutyronitrile. One example of a peroxide compound is benzoyl peroxide. Representative photoinitiators include, but are not limited to, 1-hydroxy-1-phenyl ketone, benzophenone, 2-hydroxyethyl-2-methyl-1-phenyl-propanone, 2-hydroxy-1-[4-(2-hydroxy)phenyl]-2-methyl-1-propanone, methylbenzoylformate, oxy-phosphonoyl-acetic acid 2-[2-oxo-2-phenyl-acetoxy-ethoxy]-ethyl-ester, oxy-phosphonoyl-acetic 2-[2-hydroxy-ethoxy]-ethyl ester, oxo-dimethoxy-α-phenylacetoephene, 2-benzyl-2-(dimethylamino)-1-[4-(4-morpholinyl)phenyl]-1-propanone, diphenyl(2,4,6-trimethylthio)phenyl-phosphine oxide, phosphine oxide, phenyl bis(2,6,4,6-trimethyl benzyl), bis(η2-2,4-cyclopentadien-1-yl)bis[2,6-difluoro-3-(1H-pyrrrol-1-yl)]phenyll[titanium, iodonium (4-methylphenyl)-[4-(2-methylpropyl)phenyl]-hexafluorophosphate, or a mixture of two or more thereof. In some instances, the photoinitiator is a UV initiator.

The present technology thus generally described will be understood more readily by reference to the following examples which are provided by way of illustration and are not intended to be limiting of the present technology.

EXAMPLES

Example 1

Synthesis of 1-methoxy-4-(2-methoxyethoxy)-2,5-di-tert-butyl-benzene. Scheme 1 is an illustration of the synthesis of the title compound.

Scheme 1:
2,5-di-tert-butyl-4-methoxyphenol (9 mmol) was dissolved in anhydrous N,N-dimethylformamide (10 ml). Cesium carbonate (13 mmol) and 1-bromoethyl methyl ether (9 mmol) were added to the solution. The reaction mixture was then stirred at room temperature overnight. After removal of the solvent, the residue was partitioned between dichloromethane (DCM) and aqueous NaHCO₃ (0.1 M). The organic portion was separated and dried over Na₂SO₄ and then the solvent was removed under vacuum. The crude product was chromatographed (silica, hexanes/DCM from 5:1 to 1:1) to afford pure 1-methoxy-4-(2-methoxyethoxy)-2,5-di-tert-butyl-benzene in an 85% yield. ¹H NMR (300 MHz, CDCl₃): δ ppm 6.84 (s, 1H), 6.83 (s, 1H), 4.11 (t, J = 4.5 Hz, 2H), 3.78 (m, 5H), 3.45 (s, 3H), 1.38 (s, 9H), and 1.35 (s, 9H).

Cyclic voltammograms were recorded for a 0.01M 1-methoxy-4-(2-methoxyethoxy)-2,5-di-tert-butyl-benzene in an electrolyte of 1.2M LiPF₆ in EC/EMC (3:7 by weight) using a Pt/Li/Li reference electrode at various scan rates. See FIG. 1. One pair of reversible peaks is exhibited at about 3.8 to about 4.1 V vs. Li/Li⁺. It is well known that the main electrolyte components (EC, PC, DMC, and LiPF₆) are electrochemically stable up to 4.8 V vs. Li/Li⁺ or higher. The reversible electrochemical reaction at 3.8 V to 4.1 V vs. Li/Li⁺ is therefore assigned to the reduction and oxidation peaks for the 1-methoxy-4-(2-methoxyethoxy)-2,5-di-tert-butyl-benzene.

Voltage profile overcharge test of cells using mesocarbon microbeads (MCMB) and LiFePO₄ (LFP) as electrodes, and containing 0.1 M 1-methoxy-4-(2-methoxyethoxy)-2,5-di-tert-butyl-benzene in the electrolyte of 1.2M LiPF₆ in EC/EMC (3:7 by weight) were recorded over the course of about 300 hours. See FIG. 2. The cells were charged at C/10 rate for 20 hours and then discharged to 2.2 V. The overcharge ratio (charge capacity/discharge capacity) is 100%. For each cycle, after the capacity was fully charged, the cell voltage climbed quickly to 3.8 V, where the redox overcharge protection was activated, and then the voltage was constant for the following 10 hours until discharge. The flat plateau clearly indicates that the overcharge protection was effective, and extra electricity was shunted by the reversible redox behavior of the functional electrolyte.

Capacity retention profiles of overcharge test of cells using MCMB and LFP as electrodes and containing 0.1M 1-methoxy-4-(2-methoxyethoxy)-2,5-di-tert-butyl-benzene in the electrolyte of 1.2M LiPF₆ in EC/EMC (3:7 by weight) were recorded. See FIG. 3. The charging rate was C/10, and the overcharge ratio was 100%. The difference between the charge and discharge capacity comes from the overcharge protection processes and equals the extra electricity carried by the functional electrolyte. After approximately 85 cycles, the shuttle appears to degrade.

Voltage profile overcharge test of cells using mesocarbon microbeads MCMB and LFP as electrodes and containing 0.2 M 1-methoxy-4-(2-methoxyethoxy)-2,5-di-tert-butyl-ben-

zene in an electrolyte of 1.2M LiPF₆ in EC/EMC (3:7 by weight) were recorded over the course of about 300 hours. See FIG. 4. The charging rate was C/5, and the overcharge ratio was 100%. For each cycle, after the capacity was fully charged, the cell voltage climbed quickly to 3.8 V, where the redox overcharge protection was activated, and then the voltage stayed there for the next 10 hours until discharge. The flat plateau clearly indicates that the overcharge protection was effective, and extra electricity was shunted by the reversible redox behavior of the functional electrolyte.

Capacity retention profiles of overcharge test of cells using MCMB and LFP as electrodes and containing 0.2M 1-(2-methoxyethoxy)methoxy-4-methoxy-2,5-di-tert-butyl-benzene were recorded. See FIG. 5. The charging rate was at C/10, and overcharge was 100%. The difference between the charge and discharge capacity comes from the overcharge protection processes and equals the extra electricity carried by the functional electrolytes. The electrolyte was observed to withstand more than 125 overcharge test cycles, exhibiting excellent overcharge protection.

Example 2

Synthesis of 1-methoxy-4-[2-(methoxyethoxy)ethoxy]-2,5-di-tert-butyl-benzene. Scheme 2 is an illustration of the synthesis of the title compound.

Scheme 2:

2,5-di-tert-butyl-4-methoxyphenol (9 mmol) was dissolved in anhydrous N,N-dimethylformamide (10 ml). Cesium carbonate (13 mmol) and 1-bromo-2-(methoxyethoxy)ethane (9 mmol) was added to the solution. The reaction mixture was then stirred at room temperature overnight. After removal of the solvent, the residue was partitioned between dichloromethane (DCM) and aqueous NaHCO₃ (0.1 M). The organic portion was separated and dried over Na₂SO₄ and then the solvent was removed under vacuum. The crude product was chromatographed (silica, hexanes/DCM from 5:1 to 1:1) to provide pure 1-methoxy-4-[2-(methoxyethoxy)ethoxy]-2,5-di-tert-butyl-benzene in an 87% yield. ¹H NMR (300 MHz, CDCl₃): δ ppm 6.83 (s, 1H), 6.82 (s, 1H), 4.14 (t, J = 4.5 Hz, 2H), 3.89 (t, J = 4.5 Hz, 2H), 3.80 (s, 3H), 3.72 (t, J = 4.5 Hz, 2H), 3.58 (t, J = 4.5 Hz, 2H), 3.40 (s,
Cyclic voltammograms were recorded for a solution of 0.01 M 1-methoxy-4-[2-(2-methoxyethoxy)ethoxy]-2,5-di-tert-butyl- benzene in an electrolyte of 1.2M LiPF₆ in EC/EMC (3:7 by weight), using a Pt/Li/Li three-electrode system at various scan rates. See FIG. 6. The reversible electrochemical reaction at 3.8-4.1 V vs. Li/Li' is assigned to the redox reaction of the exemplary electrolyte solvent.

Voltage profiles overcharge test of a MCMC/LiFP₆ cell containing 0.4 M 1-methoxy-4-[2-(2-methoxyethoxy)ethoxy]-2,5-di-tert-butyl-benzene in 1.2M LiPF₆ in EC/EMC (3:7 by weight) were recorded over the course of 0-200 h. See FIG. 7. The charging rate was at 2/C and the overcharge was 100%. The electrolyte was observed to provide high rate overcharge protection at 2/C charging rate.

Capacity retention profiles of MCMC/LiFePO₄ cell containing 0.4 M 1-methoxy-4-[2-(2-methoxyethoxy)ethoxy]-2,5-di-tert-butyl-benzene in 1.2M LiPF₆ in EC/EMC (3:7 by weight) were recorded. See FIG. 8. The charging rate was at 2/C and the overcharge was 100%. Under these conditions, the cells were observed to have undergone overcharge test cycles.

Capacity retention profiles of LiFePO₄ cells using an electrolyte of 2:1 [1,2M LiPF₆ in EC/EMC (3:7 by weight)] to [1-methoxy-4-[2-(2-methoxyethoxy)ethoxy]-2,5-di-tert-butyl-benzene] by weight were recorded. See FIG. 9. The cells were cycled at room temperature from 1.5 V to 2.1 V at C/10 rate. Despite the degradation of the capacity, the cyclic performance clearly indicated that 1-methoxy-4-[2-(2-methoxyethoxy)ethoxy]-2,5-di-tert-butyl-benzene can be used as a co-solvent in the electrolyte system.

While certain embodiments have been illustrated and described, it should be understood that changes and modifications can be made therein in accordance with ordinary skill in the art without departing from the technology in its broader aspects as defined in the following claims.

The embodiments, illustratively described herein, may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for example, the terms "comprising," "including," "containing," etc., shall be read expansively and without limitation. Additionally, the terms and expressions employed herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that many modifications are possible within the scope of the claimed technology. Additionally, the phrase "consisting essentially of will be understood to include those elements specifically recited and those additional elements that do not materially affect the basic and novel characteristics of the claimed technology. The phrase "consisting of excludes any element not specified.

The present disclosure is not to be limited in terms of the particular embodiments described in this application. Many modifications and variations can be made without departing from its spirit and scope, as will be apparent to those skilled in the art. Functionally equivalent methods and compositions within the scope of the disclosure, in addition to those enumerated herein, will be apparent to those skilled in the art from the foregoing descriptions. Such modifications and variations are intended to fall within the scope of the appended claims. The present disclosure is to be limited only by the terms of the appended claims, along with the full scope of equivalents to which such claims are entitled. It is to be understood that this disclosure is not limited to particular methods, reagents, compounds compositions or biological systems, which can of course vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting.

In addition, where features or aspects of the disclosure are described in terms of Markush groups, those skilled in the art will recognize that the disclosure is also thereby described in terms of any individual member or subgroup of members of the Markush group.

As will be understood by one skilled in the art, for any and all purposes, particularly in terms of providing a written description, all ranges disclosed herein also encompass any and all possible subranges and combinations of subranges thereof. Any listed range can be easily recognized as sufficiently describing and enabling the same range being broken down into at least equal halves, thirds, quarters, fifths, tenths, etc. As a non-limiting example, each range discussed herein can be readily broken down into a lower third, middle third and upper third, etc. As will also be understood by one skilled in the art, all language such as "up to," "at least," "greater than," "less than," and the like, include the number recited and refer to ranges which can be subsequently broken down into subranges as discussed above. Finally, as will be understood by one skilled in the art, a range includes each individual member.

All publications, patent applications, issued patents, and other documents referred to in this specification are herein incorporated by reference as if each individual publication, patent application, issued patent, or other document was specifically and individually incorporated to be incorporated by reference in its entirety. Definitions that are contained in text incorporated by reference are excluded to the extent that they contradict definitions in this disclosure.

Other embodiments are set forth in the following claims.

What is claimed is:

1. A functional electrolyte solvent comprising a compound of formula

![Chemical Structure](image)

wherein:

- R² is H, F, Cl, Br, I, alkyl, or a polyether group; and
- R³ is H, F, Cl, Br, I, alkyl, or a polyether group.

2. The functional electrolyte solvent of claim 1, wherein the compound has the structure
3. The functional electrolyte solvent of claim 1, wherein the compound has the structure:

4. The functional electrolyte solvent of claim 1, wherein the compound is:

5. The functional electrolyte solvent of claim 1, wherein the compound is:

6. An electrolyte comprising:

   - The functional electrolyte solvent of claim 1; and
   - An alkali metal salt.

7. The electrolyte of claim 6, wherein the functional electrolyte solvent is a redox active material and has a redox potential of 3 to 5 V.

8. The electrolyte if claim 6, wherein the functional electrolyte solvent is 1-methoxy-4-(2-methoxyethoxy)-2,5-di-tert-butyl-benzene, 1-methoxy-4-[2-(2-methoxyethoxy)ethoxy]-2,5-di-tert-butyl-benzene, or a mixture thereof.

9. The electrolyte of claim 6, wherein the concentration of the functional electrolyte solvent in the electrolyte is from 0.0005 wt % and 60 wt %.

10. The electrolyte of claim 6, wherein the alkali metal salt is a lithium salt.

11. The electrolyte of claim 6, wherein the alkali metal salt is Li[(C₆H₅)₂]B, Li[(C₆H₅)O]BF₄, LiClO₄, LiBF₄, LiAsF₆, LIPF₆, LiCF₃SO₃, Li[(CF₃SO₂)₂N, Li[(CF₃SO₂)₂]C, LiN(SO₂C₆H₅)₂, lithium alkyl fluorophosphates, or a mixture of any two or more thereof.

12. The electrolyte of claim 6 further comprising a polar aprotic solvent.

13. The electrolyte of claim 12, wherein the polar aprotic solvent is selected from ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, dimethyl ether, gamma butyrolactone, or a mixture of any two or more thereof.

14. The electrolyte of claim 6, wherein the alkali metal salt is other than Li[(C₆H₅)₂]B, Li[(C₆H₅)O]BF₄, and the electrolyte further comprises about 0.001 wt % to about 8 wt % of an electrode stabilizing additive that is Li[(C₆H₅)₂]B, Li[(C₆H₅)O]BF₄, or a mixture thereof.

15. The electrolyte of claim 6 further comprising an electrode stabilizing additive that is a substituted or unsubstituted spirocyclic hydrocarbon containing at least one oxygen atom and at least one alkyl or alkyne group.

16. An electrochemical device comprising:

   - a cathode
   - an anode; and
   - An electrolyte of claim 6.

17. The electrochemical device of claim 16, wherein the device is a lithium secondary battery; the cathode is a lithium metal oxide cathode; the anode is a carbon or lithium metal anode; and the anode and cathode are separated from each other by a porous separator.

18. An electrolyte comprising:

   - An alkali metal salt; and
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

In the Claims

In Column 24, Claim 8, Line 6, remove “(2-methoxyethoxy)” and replace with
--(2-methoxyethoxy)--.

In Column 24, Claim 11, Line 15, remove “Li(CF₃SO₂)₂N,” and replace with --Li(CF₃SO₂)₂N,--.

In Column 24, Claim 18, Lines 46 and 47, remove “(2-methoxyethoxy)” and replace with
--(2-methoxyethoxy)--.

In Column 24, Claim 18, Line 48, remove “(2-ethoxyethoxy)” and replace with --(2-ethoxyethoxy)--.

In Column 24, Claim 18, Line 50, remove “methoxyethoxy)” and replace with --methoxyethoxy)--.

In Column 24, Claim 18, Line 52, remove “methoxyethoxy)” and replace with --methoxyethoxy)--.

In Column 24, Claim 18, Line 54, remove “(2-methoxyethoxy)” and replace with
--(2-methoxyethoxy)--.

Signed and Sealed this
Eighteenth Day of August, 2015

Michelle K. Lee
Director of the United States Patent and Trademark Office